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CHEMICAL DERIVATIZATION OF AN ARRAY OF THREE GOLD
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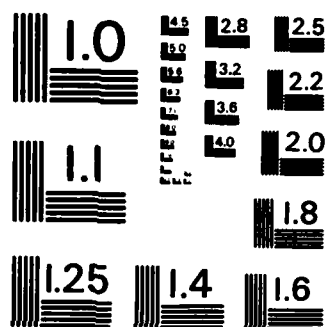
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An array of three Au microelectrodes each 3 μm wide x 140 μm long x 0.12 μm thick and separated from each other by 1.4 μm can be derivatized with polypyrrole in a manner such that an electrical connection is made between the three electrodes when the polypyrrole is in its oxidized and conducting state. Typical coverage of polypyrrole is 10^{-7} mol/cm² of exposed Au. Properties resembling those of a solid state transistor can be obtained when the device is immersed in CH₃CN/0.1 M [n-Bu₄]ClO₄ solution. Taking one electrode to be the "gate" and the other two electrodes to be the "source" and "drain", the resistance between the source and drain can be altered dramatically by varying the potential of the gate. The current between source and drain is a function of potential between source and drain, as expected. The key result is that the small signal needed to turn the polypyrrole from its reduced and insulating state to the oxidized and conducting state can be amplified. In absolute terms, the charge needed to turn on the device is some fraction of 10^{-8} C to give a steady-state drain current of -4×10^{-5} C/s at a source-drain potential of 0.2 V.

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TECHNICAL REPORT NO. 1

"CHEMICAL DERIVATIZATION OF AN ARRAY OF THREE GOLD
MICROELECTRODES WITH POLYPYRROLE:
FABRICATION OF A MOLECULE-BASED TRANSISTOR"

by

Henry S. White, Gregg P. Kittlesen and Mark S. Wrighton

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-Communication to the Editor-

CHEMICAL DERIVATIZATION OF AN ARRAY OF THREE GOLD MICROELECTRODES WITH
POLYPYRROLE: FABRICATION OF A MOLECULE-BASED TRANSISTOR

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Abstract

An array of three Au microelectrodes each 3 μm wide x 140 μm long x 0.12 μm thick and separated from each other by 1.4 μm can be derivatized with polypyrrole in a manner such that an electrical connection is made between the three electrodes when the polypyrrole is in its oxidized and conducting state. Typical coverage of polypyrrole is 10^{-7} mol/cm² of exposed Au. Properties resembling those of a solid state transistor can be obtained when the device is immersed in CH₃CN/0.1 M [n-Bu₄]ClO₄ solution. Taking one electrode to be the "gate" and the other two electrodes to be the "source" and "drain", the resistance between the source and drain can be altered dramatically by varying the potential of the gate. The current between source and drain is a function of potential between source and drain, as expected. The key result is that the small signal needed to turn the polypyrrole from its reduced and insulating state to the oxidized and conducting state can be amplified. In absolute terms, the charge needed to turn on the device is some fraction of 10^{-8} C to give a steady-state drain current of $\sim 4 \times 10^{-5}$ C/s at a source-drain potential of 0.2 V.

~~We wish to report~~ the fabrication of a chemically derivatized microelectrode array that can function as a transistor when immersed in an electrolyte solution. The key finding is that ~~we~~ have been able to show that a small signal (charge) needed to turn on the device can be amplified. The device to be described mimics the fundamental characteristics of a solid state transistor,¹ since the resistance between two contacts can be varied by a signal to be amplified. Figure 1 illustrates the device fabricated and the external circuit elements needed to characterize it. The chemical transistor is the set of three (drain, gate, and source) Au microelectrodes covered with polypyrrole. Three features are essential: (1) the three independent Au microelectrodes are closely spaced, 1.4 μm apart, allowing an easily measurable current to pass between the source and drain when V_D is significant and V_G is above the threshold, V_T ; (2) the polypyrrole exhibits a sharp change in conductivity upon oxidation;² the potential at which this occurs is V_T ; and (3) each of the microelectrodes can be individually contacted. The input signal to the gate to be amplified is that needed to oxidize the polypyrrole.³ Importantly, V_T and the magnitude of signal needed to achieve V_T can be manipulated by variation of the molecule-based material. Conceptually, the device described here stems from the molecule-based "diode" and "triode" fabricated by derivatizing a macroscopic electrode with a redox polymer and a porous metal outer contact.⁴ Additionally, the device represented in Figure 1 is a type of "chemiresistor"⁵ where an electrical signal can change the resistance of the chemical layer.

Experiments have been carried out using "chips" consisting of a microelectrode array of eight individual Au electrodes deposited on a 1 μm thick SiO_2 insulator grown on <100> Si. Each of the eight microelectrodes can be addressed independently and is generally 3 μm wide x 140 μm long x 0.12 μm thick

separated from each other by $1.4 \mu\text{m}$.⁶ Microelectrodes can be functionalized with controlled amounts of polypyrrole by oxidizing 50 mM pyrrole in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ at +0.8 V vs. SCE, as described for macroscopic electrodes.² Microelectrodes derivatized in this manner can be characterized by cyclic voltammetry in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$, revealing the typical response expected for surface-bound polypyrrole.²

When the microelectrode array is derivatized with a sufficiently large coverage of polypyrrole the individual microelectrodes can be electrically connected by the polymer.⁶ The experimental evidence for this is that all of the connected electrodes show the same cyclic voltammetry response (peak position, shape, and area), when measured individually and when they are externally connected together and driven as one electrode. When three microelectrodes are connected together with the polypyrrole as in Figure 1 the charge associated with the oxidation and reduction of the bound polymer is of the order of 10^{-2} C/cm^2 of exposed Au. Examination of derivatized microelectrode arrays by scanning electron microscopy confirms the presence of the polymer.

Characterization of a derivatized three electrode array shows that a transistor characteristic can be obtained, Figure 2.⁷ In this set of measurements the two outer electrodes are wired as source and drain and the middle electrode is the gate, Figure 1. Figure 2 shows the current between source and drain, I_D , as a function of the potential between source and drain, V_D , at various fixed gate potentials, V_G . When V_G is held at a negative potential where the polypyrrole is expected to be insulating the device is "off" and I_D is small at values of $V_D < 0.5 \text{ V}$. When V_G is moved to potentials more positive than the oxidation potential of polypyrrole, $\sim -0.2 \text{ V vs. SCE}$, the device "turns on" and a significant steady-state value of I_D can be observed for modest values of V_D . We take the

redox potential of polypyrrole to approximate the value of V_T , the gate potential at which the device starts to turn on. For V_G more positive than V_T the value of I_D increases at a given value of V_D , in a manner consistent with increasing conductivity of polypyrrole with an increasing degree of oxidation. At sufficiently positive values of V_G , $\geq +0.5$ V vs. SCE, I_D becomes insensitive to further positive movement of V_G at a given value of V_D , a result consistent with measurements⁵ of the resistance of the oxidized polypyrrole coated on a microelectrode array. We typically use only a small range of V_D values because we seek to minimize electrochemical reactions at the source/polymer and drain/polymer interfaces. All measurements are for deoxygenated solutions, owing to problems stemming from irreversible oxidation of the polymer. However, in the absence of O_2 good durability (several days of use) can be achieved. Shelf-life in the dry state exceeds one week for derivatized arrays.

For the devices studied, some fraction of 10^{-8} C of charge is required to obtain the maximum steady-state value of I_D at $V_D = 0.2$ V; the value of I_D achievable with the device represented in Figure 1 is $\sim 4 \times 10^{-5}$ C/s. Thus, a small signal to the gate can be amplified in much the same way that a small electrical signal can be amplified with a solid state field effect transistor.¹ A major difference, of course, between the solid state device and the molecule-based device is that the turn on/turn off time in the molecule-based system depends on the rate of a chemical reaction whereas no chemical reactions take place in the solid state devices. For the devices fabricated the on-off time is of the order of 10 s; the curves in Figure 2 are steady-state curves. For the molecule-based system the properties such as V_T and minimum turn on signal can be adjusted with rational variation in the monomer used to prepare the polymer. Smaller dimensions can lead to faster switching times and different molecule-based gate materials may have superior rates of switching compared to polypyrrole.

The molecule-based transistor reported here has no immediate practical application. The fundamental accomplishment is the demonstration of the synthesis of an interfacial chemical system that has a specific function. There is presently considerable interest in interfacing microelectronic devices with chemical and biological systems for sensor applications⁵ and in "molecular electronics" in general.⁸ Our work establishes that principles learned from the study of polymer-modified macroscopic electrodes^{4,9-14} can be applied in a much smaller dimensional regime to achieve specific functions where the molecule-based material is the active element.

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3. The particular arrangement shown in Figure 1 has been used for clarity. Any one of the three electrodes could be used as a "gate" with the other two being "source" and "drain". Use of the gate electrode allows a quantitative determination of the amount of charge necessary to turn the polypyrrole from insulating (off) to conducting (on). Thus, the "gate" allows a quantitative assessment of the behavior of a two electrode device where the input "signal" could be a redox reagent that equilibrates with the polypyrrole to turn it on. The arrangement in Figure 1 explicitly differs from solid state transistors where both the gate and drain potentials are fixed relative to the source.¹ The crucial fact is that polypyrrole undergoes a dramatic change in conductivity upon transfer of a small amount of charge.
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7. A 3 V battery and voltage divider were used to vary V_D from 0.0 to 0.2 V. The gate electrode was connected in a conventional 3 electrode potentiostatic arrangement employing a Pine Model RDE 3 bipotentiostat. A Pt wire and saturated calomel electrode, SCE, were used as the counter and reference electrodes, respectively. I_D was measured by recording the potential drop across a 100^7 resistor resulting from the steady-state current between the source and drain electrode. All curves are for the microelectrode array, Pt and SCE electrodes immersed in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ at 25°C under N_2 .
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Figure Captions

Figure 1. Cross-sectional view of the device fabricated and representation of the circuit elements used to characterize it. The SiO₂ layer is ~1 μm thick and is on a ~0.3 mm thick <100> Si substrate. The source, gate, and drain are Au, ~3 μm wide x 140 μm long x 0.12 μm thick coated with ~10⁻⁷ mol/cm² of polypyrrole. When characterized, the derivatized microelectrode array, counter and reference electrodes are immersed in electrolyte solution.

Figure 2. Output characteristics of the transistor shown in Figure 1 in CH₃CN/0.1 M [n-Bu₄N]ClO₄.

